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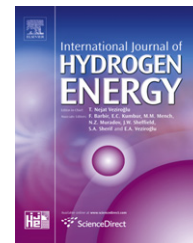
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Tantalum carbide as a novel support material for anode electrocatalysts in polymer electrolyte membrane water electrolyzers

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ABSTRACT

Iridium oxide (IrO₂) currently represents a state of the art electrocatalyst for anodic oxygen evolution. Since iridium is both expensive and scarce, the future practical application of this process makes it essential to reduce IrO₂ loading on the anodes of PEM water electrolyzers. In the present study an approach to utilising a suitable electrocatalyst support was followed. Of the materials selected from a literature review, TaC has proved to be stable under the conditions of the accelerated stability test proposed in this study. The test involved dispersing each potential support material in a mixture of trifluoromethanesulfonic acid (TFMSA) and hydrogen peroxide at 130 °C. The liquid phase was subsequently analysed using ICP-MS with respect to the occurrence of ions potentially originating from the support material tested. The TaC support selected was additionally characterised by thermogravimetric and differential thermal analysis to prove its thermal stability. A modified version of the Adams fusion method was used to deposit IrO₂ on the support surface. A series of electrocatalysts was prepared with a composition of (IrO₂)_x(TaC)_{1-x}, where x represents the mass fraction of IrO₂ and was equal to 0.1, 0.3, 0.5, 0.7, 0.9 and 1. The thin-film method was used for electrochemical characterisation of the electrocatalysts prepared. SEM–EDX analysis, X-ray diffraction, N₂ adsorption (BET) and powder conductivity measurements were used as complementary techniques to complete characterisation of the electrocatalysts prepared. The electrocatalysts with $x \geq 0.5$ showed stable specific activity. This result is consistent with the conductivity measurements.

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1. Introduction

Hydrogen is currently considered to be one of the most important future energy carriers that can be used to store

energy from renewable sources. Energy stored in hydrogen can be converted back into electricity for use in the distribution grid or in technologies such as uninterrupted power sources and hydrogen-powered cars [1,2].

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Electrolysis is a viable method for the production of carbon-free hydrogen. Although alkaline electrolysis is currently mainly used for this purpose, acidic polymer electrolyte membrane water electrolyzers (PEMWEs) are attracting great interest as a promising new alternative technology [3]. The advantages of PEMWEs over alkaline electrolyzers primarily lie in their higher efficiency and higher process intensity [4]. However, the major drawback of the PEMWEs is the need for electrocatalysts based on platinum group metals. This especially concerns the anode, where so far only iridium-based electrocatalysts are known to withstand the severe conditions that occur at the PEMWE anode during the oxygen evolution reaction (OER) [5]. The highly acidic environment at the PEMWE anode, together with a polarisation of ≥ 1.5 V and temperatures of 80–200 °C, can be tolerated by few materials for any length of time [6]. Whereas RuO₂ has the lowest overpotential for OER, IrO₂ is far more stable and is, therefore, used exclusively as an oxygen evolution electrocatalyst [7].

Unfortunately, iridium is not only expensive (1085 USD/troy ounce as of 1 December 2011 [8]), but also scarce, being about 50 times less abundant than platinum [9]. In 2010, the electrochemical industry accounted for approximately one quarter of its total demand [10]. Consequently, it is crucial to reduce the amount of IrO₂ in PEMWEs if this technology is to become more widely used. One approach to lowering the amount of IrO₂ in PEMWEs involves the use of an electrocatalyst support; namely, a non-reactive material that is preferably both inexpensive and readily available [11]. The role of the electrocatalyst support in this process can be three-fold. Firstly, it enables synthesis of smaller IrO₂ crystallites because it offers a number of crystallisation centres during IrO₂ deposition and at the same time reduces the probability of their agglomeration. Secondly, supported particles are larger in size than unsupported particles. This is advantageous during preparation of the catalytic layer: larger particles do not penetrate deeper into the layer, but stay in good contact with the polymer electrolyte membrane. As a consequence, higher efficiency of electrocatalyst utilisation can be achieved. Thirdly, the interaction of the electrocatalyst with the support may influence the electrocatalytic properties of the resulting material due to synergic effects.

Building on the work of Nikiforov et al., who have shown that SiC–Si can be used as an electrocatalyst support [12], this work focused on ceramic materials. Four ceramic materials potentially suitable for this application were identified in the literature [13]: TaC, Si₃N₄, WB and Mo₂B₅. These materials were chosen because they are stable in harsh environments and also, in some cases, are electrically conductive. To select the most stable material in this group, a quick and easy preliminary stability test was developed, based on exposing the prospective support material to a mixture of trifluoromethanesulfonic acid (TFMSA) and hydrogen peroxide at 130 °C. After a defined time, the liquid phase is analysed for the presence of ions originating from the dissolved support material. TFMSA was chosen because it provides a high level of acidity without any unwanted complexing or chelating effects. The hydrogen peroxide provides an oxidative environment to simulate the anodic polarisation in a PEMWE. Overall, the conditions chosen were harsher than conditions in a PEMWE because this is an accelerated test which should

provide the required information on material stability in a relatively short time.

Electronic conductivity represents another important parameter that influences electrocatalyst performance. At this point a distinction has to be made between the conductivity of the support itself and of the entire composite material, consisting of the support and IrO₂. It should be borne in mind that the conductivity of IrO₂ alone is sufficient for the operation of a PEMWE when IrO₂ covers most of the support, i.e. when it exceeds the percolation level. Therefore, even a non-conductive support may be acceptable for the process. However, it is necessary to use high IrO₂ loading and at the same time a support material with a relatively low specific surface area to allow formation of a coherent conductive surface film of IrO₂. Finally, the electrical conductivity of the support is very welcome since it can reduce the ohmic drop in the PEMWE [14], but it is not a critical quality.

Several methods for the synthesis of electrocatalysts have been described in the literature. The most common is the Adams fusion method [15], which produces metal oxides [12,16–20]. The other methods used are the polyol method (also known as the colloid method) [16,17,19], simple thermal decomposition of the corresponding metal chlorides [21], and chemical reduction [22]. The polyol method and chemical reduction are usually followed by the oxidation of the resulting metal particles, either anodically or by simple calcination in air.

In the present work a modified version of the Adams fusion method was used for the synthesis of IrO₂ supported on TaC. This method was selected because it provides IrO₂ particles straight from the synthesis and because it allows direct comparison with the results of the preceding work [12]. The electrochemical activity of the prepared supported IrO₂ electrocatalysts was compared with that of an unsupported IrO₂ electrocatalyst.

Thus, for the first time, the use of TaC as a support material for IrO₂-based electrocatalysts for PEMWEs is reported.

2. Experimental

2.1. Support stability testing

2.1.1. Starting materials

Based on a literary review, the following materials were tested as potential electrocatalyst supports: TaC (Sigma–Aldrich, 99%), Si₃N₄ (Goodfellow, >85%), WB (Alfa Aesar, 99%) and Mo₂B₅ (Cerac Inc., 99.5%). To remove any surface contamination, approximately 200 mg of each material was first etched in 50 mL of boiling 2% HCl for 15 min. After cooling down to room temperature, each suspension was washed five times with demineralised water on a centrifuge to remove chlorides. Final washing was followed by evaporation under argon.

2.1.2. Chemical stability test of the support

A mixture of the four support materials was created by taking 50 mg of each one. Then, 5 mL of concentrated TFMSA (Sigma–Aldrich, 98%) was poured into the mixture before 1.67 mL of 30% hydrogen peroxide was added drop-wise. The mixture was kept stirred at 130 °C in a glass vessel, at the top of which

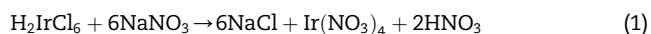
a reflux condenser was attached. After 48 h, the mixture was cooled down to room temperature and diluted to 50 mL with demineralised water. The remaining powder was separated using a centrifuge and a 5 mL aliquot was taken as a sample. To prevent the ions from precipitating, 100 mg of NaF was added to the sample and the mixture was heated in a closed vessel at 80 °C for 1 h.

2.1.3. ICP-MS analysis

The sample containing the dissolved ions was analysed using a Perkin–Elmer Elan 6000 ICP-MS with a dual-stage detector with a high-concentration setting. All standards for the calibration line were purchased from Fluka. The calibration line was designed with a lower limit corresponding to 0.1% of the dissolved support material.

2.2. Electrocatalysts preparation

From the stability test, TaC was chosen as the preferred electrocatalyst support. The electrocatalysts with varying content of IrO₂ were prepared, using a modified version of the Adams fusion method [15]. The chemical reactions (1, 2), corresponding to the Adams fusion suggested by Marshall et al. [16], are shown below:



The TaC support and a metal precursor (H₂IrCl₆·4H₂O, Alfa Aesar, 99%) were added to 10 mL of isopropanol and stirred for 1 h to ensure complete dissolution of the iridium salt. After the addition of finely ground NaNO₃ (16.7 × molar excess), the salt mixture was heated in air to 70 °C and evaporated to dryness. Then, the mixture was placed into a furnace and heated up to 500 °C at a rate of 250 °C/h. It remained at 500 °C for 1 h before cooling to room temperature overnight. The fused product was washed six times with demineralised water and separated on a centrifuge. Finally, the powder was dried in air at 90 °C.

Electrocatalysts were prepared with concentrations of 10, 30, 50, 70, 90 and 100 wt.% IrO₂ and are labelled as (IrO₂)_x(TaC)_{1-x}, where x is the mass fraction of IrO₂. Like all Adams fusion processes, our modified version provided a yield of almost 100% [16]. The modified Adams fusion process was also applied to pure TaC to see if the process had any impact on its properties.

2.3. Physico-chemical characterisation

Scanning electron microscope (SEM) images of the electrocatalysts were taken on a JEOL JSM-5910 (10 kV acceleration voltage, 7 mm working distance). The SEM was equipped with an energy-dispersive X-ray spectrometer (EDX) that was used to collect an element map of the electrocatalyst. The EDX itself consisted of an Oxford Instruments X-Max silicon drift detector (SDD) controlled by Oxford Instruments INCA software.

A Netzsch STA 409 PC was used to perform thermogravimetric and differential thermal analysis on the TaC. In

a synthetic air atmosphere (20.8% O₂, 79.2% N₂, AGA GAS AB), the temperature ramp was increased from room temperature to 1000 °C at a rate of 5 °C/min.

All electrocatalyst samples were analysed on a Huber D670 X-ray powder diffractometer (Cu–Kα, α = 1.5405981 Å).

Using a Micromeritics Gemini 2375 analyser, the specific surface areas of the electrocatalysts and the TaC were measured by the Brunauer–Emmett–Teller (BET) method.

In accordance with a method previously used by our group [12], powder conductivity measurements were performed in a small acrylic cylinder with a through hole (inner diameter 3 mm) into which two opposing copper pistons retracted. The powder was compressed in the cell by clamping the outer ends of both pistons in a micrometre. The micrometre axle was tightened to a constant torque of 0.2 Nm. Then, a Versa-STAT 4 potentiostat running VersaStudio 2.0 software (Princeton Applied Research) was used to determine the conductivity of the powder samples. Conductivity of each sample was measured for 4–5 layer thicknesses. The conductivity value was obtained from the slope of the dependence of its resistance on thickness.

2.4. Electrochemical characterisation

To evaluate the electrochemical performance of the electrocatalysts, working electrodes were prepared using the thin-film method [23]. A glassy-carbon disk embedded in PTFE casing was used as the working electrode. The exposed part consisted of a 5 mm diameter circle onto which was pipetted 8 μL of electrocatalyst dispersion in demineralised water, the dispersion having been ultrasonically homogenised for 1 h beforehand. For all samples, the IrO₂ concentration in the dispersion was 1 mg per mL. The electrocatalyst loading on the working electrode was 40 μg of IrO₂/cm². The electrocatalyst layer was fixed with an 8 μL drop of diluted Nafion solution (1 mg dry basis/mL) in isopropanol/demineralised water (3:1, w/w).

Electrochemical measurements were carried out in a three-necked electrochemical cell with a platinum wire counter-electrode and a saturated calomel reference electrode (SCE) connected to the cell via a liquid junction. All potentials in this article refer to this electrode. The electrolyte was 0.5 M H₂SO₄ at room temperature (23 ± 2 °C).

A VersaSTAT 4 potentiostat running VersaStudio 2.0 software (Princeton Applied Research) was used for all electrochemical experiments. Cyclic voltammetry experiments were conducted between 0 and 1.2 V at scan rates of 500, 300, 100 and 50 mV/s. Tafel experiments were performed from 1.1 to 1.3 V at a scan rate of 1 mV/s.

3. Results and discussion

3.1. Support stability test

The solution analysis detected the most unstable compound of the four analysed to be Mo₂B₅, which had the highest dissolution extent of 93.3%. On the other hand only 3.3% of WB dissolved in 48 h. This material thus proved to be relatively stable under test conditions. But although such a relatively

slow dissolution was detected, it may represent a problem in PEMWE, where the material must be able to withstand thousands of runtime hours. According to the analysis, only 0.5% of Si_3N_4 dissolved within 48 h of exposure. This suggests that it is highly stable. Additionally, the effect of the nitrogen present in the air and Si from the glass reaction vessel walls on the analysis results has to be considered. This material thus represents a promising candidate for the electrocatalyst support. But the results of the ICP-MS analysis showed that TaC, with no ions detected in the solution (Table 1), was the most resistant material of those under study. Therefore TaC was chosen as the support for IrO_2 in this study.

To confirm the thermal stability of TaC selected as the electrocatalyst support, TGA and DTA curves were recorded for the as-received sample of this material (Fig. 1). TaC showed a steady weight gain above 200 °C as it was oxidised to Ta_2O_5 . At 330 °C, oxidation to Ta_2O_5 had reached an extent of 1 wt.%. More rapid oxidation started at temperatures above 600 °C and finished at 790 °C. At this point TaC was quantitatively oxidised to Ta_2O_5 . Theoretically, 100% TaC oxidised to Ta_2O_5 should show a weight gain of 14.5 wt.%. A gain of 14.9 wt.%, calculated as the difference between the lowest and highest recorded mass, was observed within this study. This discrepancy may have been caused by the non-stoichiometric composition of the TaC used [24]. Thus, TaC appears to be highly stable within the temperature range foreseen for the PEMWE, i.e. below 200 °C. The situation is less clear with respect to electrocatalyst synthesis by Adams fusion. Here Ta_2O_5 formation has to be considered as a possible option.

3.2. Physico-chemical characterisation

3.2.1. X-ray diffraction

X-ray diffractograms of series of the electrocatalysts based on TaC supported IrO_2 are shown in Fig. 2. As expected, all diffractograms show well-defined lines of IrO_2 and TaC (except the one for pure IrO_2). Besides these lines, an additional component, identified as NaTaO_3 , was observed in the diffraction spectra of the supported electrocatalyst: it is a perovskite-type semiconductor with a band gap of 4.0 eV [25]. Its origin lies in oxidation of the TaC support by NaNO_3 during the Adams fusion process. Diffraction lines of this component are scarcely visible for the electrocatalyst containing 90% of IrO_2 . This is due to its small content in this particular sample. However, closer inspection reveals a definite diffraction line at $2\theta = 22.8^\circ$.

Table 1 – Extent of dissolution of tested materials in TFMSA/ H_2O_2 (3:1, w/w). Temperature 130 °C, duration 48 h.

Compound	Dissolved portion (%)
TaC	Below quantification limit (<0.1)
Si_3N_4	0.5
WB	3.3
Mo_2B_5	93.3

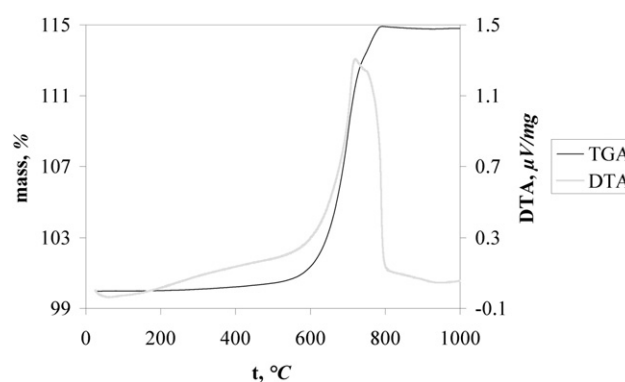


Fig. 1 – Thermogravimetric and differential thermal analysis curves of TaC in synthetic air. Heating rate 5 °C/min.

The Scherrer equation [26] was used to calculate the average crystallite size of the IrO_2 in the electrocatalysts for different contents of IrO_2 (Fig. 3); the IrO_2 peak located at $2\theta = 28^\circ$ (110) was used for this purpose (see inset in Fig. 2). The accuracy of this size determination was better than $\pm 10\%$. The peak recorded for the 10 wt.% IrO_2 electrocatalyst was too weak. Therefore, the crystallite size could not be determined for this composition.

The data shown in Fig. 3 have to be discussed as two sets of data obtained under different conditions. Whereas the pure IrO_2 was synthesised in an initially homogeneous phase of molten salts, samples with the electrocatalyst support represent a heterogeneous reaction system where the support participates in the synthesis as a solid phase. Pure IrO_2 has to overcome a significant initiation barrier during nucleation of the first crystallites in the homogeneous liquid phase. Once the nucleation centres have formed, it is energetically favourable for the IrO_2 phase to deposit continuously on already existing crystallites. On the other hand, the presence of the electrocatalyst support introduces a high number of potential IrO_2 nucleation centres on the defects of its structure. Logically, pure IrO_2 forms larger crystallites when compared to the supported electrocatalysts.

Another interesting observation is that the smallest crystallites were observed for the 90 wt.% IrO_2 electrocatalyst. The higher the concentration of the support, the larger the crystallite size with pronounced enlargement starting at 50 wt.% IrO_2 . The same trend has been reported elsewhere [16]. Such behaviour may be explained by the driving force for the nucleation of the IrO_2 phase: for the 90 wt.% IrO_2 electrocatalyst, the concentration of the iridium oxide precursor in the reaction system is the highest, resulting in the formation of the highest number of nucleation centres. Therefore, it leads to the formation of smaller crystallites. With decreasing content of the iridium oxide precursor, this driving force, and thus the number of nucleation centres formed, decreases.

3.2.2. SEM and EDX analysis

SEM pictures of the TaC supported electrocatalyst containing 50 wt.% IrO_2 (Fig. 4) and the pure IrO_2 electrocatalyst (not shown) were recorded. The morphology of the two samples is similar, both showing IrO_2 present in the form of

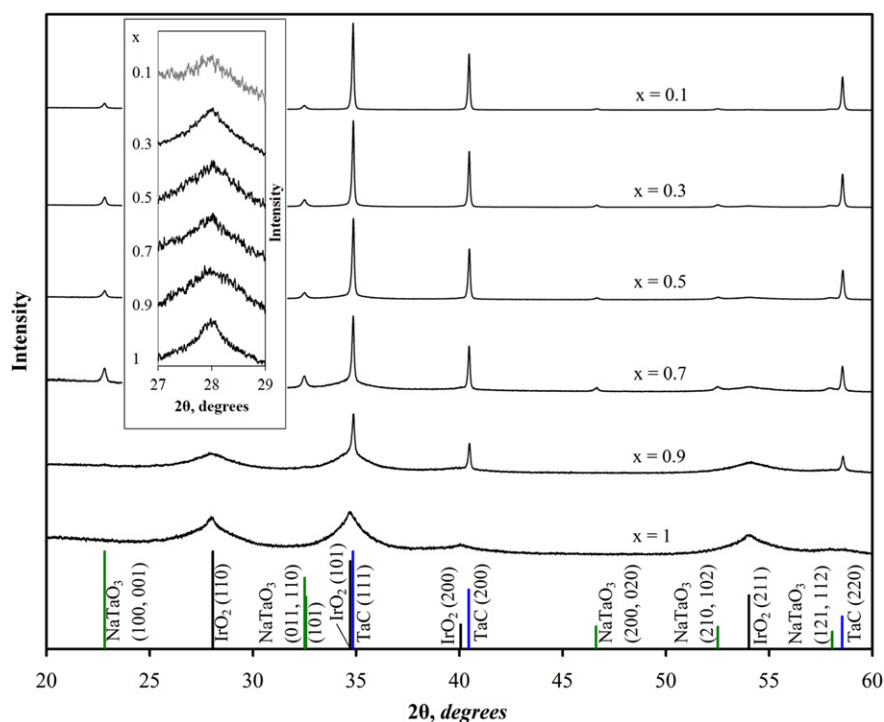


Fig. 2 – X-ray diffractograms of electrocatalysts prepared with mass-based composition $(\text{IrO}_2)_x(\text{TaC})_{1-x}$. Figures in parentheses indicate corresponding h, k, l Miller indices of the crystal planes. The inset graph shows zoomed region around 28° where the characteristic peak of IrO_2 has been used to calculate the crystallite size.

agglomerates ranging from 50 to 500 nm in diameter. Owing to the rounded shape of the agglomerates, the surface-to-mass ratio is relatively high, enabling high electrocatalytic activity. The homogeneity of the IrO_2 distribution is confirmed by the EDX element map (Fig. 5).

The sodium content was determined to confirm the presence of the NaTaO_3 phase formed during Adams fusion and identified by XRD experiments. Homogeneous distribution over the support surface was proven (Fig. 5).

3.2.3. Specific surface area

Of the materials studied, pure IrO_2 had the highest specific surface area (SSA) of $121 \text{ m}^2/\text{g}$, while pure TaC had the lowest

one at only $2.4 \text{ m}^2/\text{g}$ for TaC after synthesis (Fig. 6) and $0.7 \text{ m}^2/\text{g}$ as-received (not shown). The remaining samples followed the rule of mixing, i.e. the SSA was linearly dependent on the content of IrO_2 in the sample. No relation between crystallite size and SSA was observed. This is further confirmed by the SSA of the IrO_2 part in the supported electrocatalyst calculated from the known SSA of the support and composition of the sample. The results (Fig. 6) indicate no dependence on the size of the IrO_2 crystallites. From the SEM image (Fig. 4) and XRD analysis (Fig. 3), it can be concluded that the individual

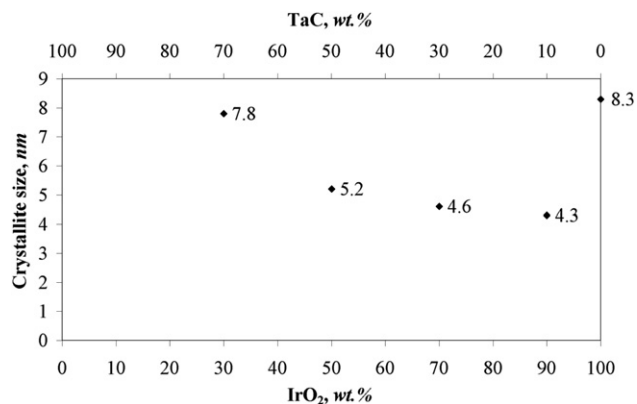


Fig. 3 – Average crystallite sizes of the prepared electrocatalysts as calculated from the XRD spectra.

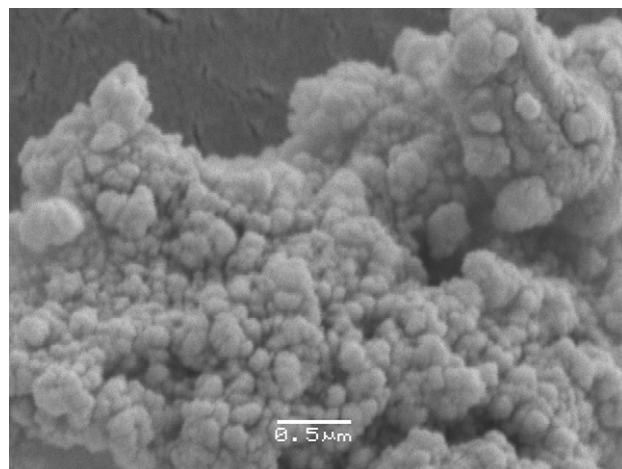
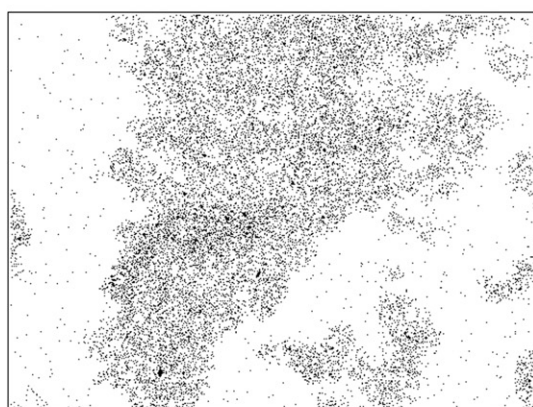
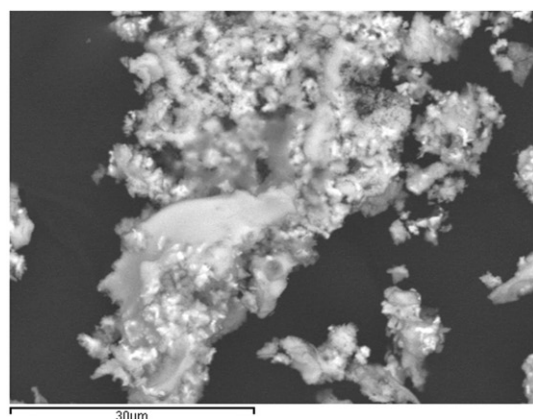
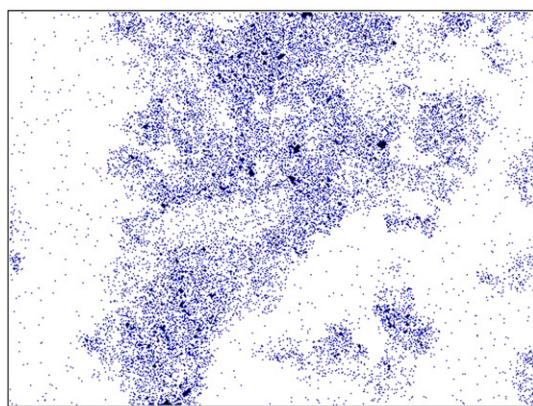


Fig. 4 – Detailed SEM image of 50 wt.% IrO_2 electrocatalyst. Accelerating voltage 10 kV, working distance 7 mm.



Ir La1



Ta La1



Na Ka1_2

Fig. 5 – SEM–EDX element map for 50 wt.% IrO₂ electrocatalyst.

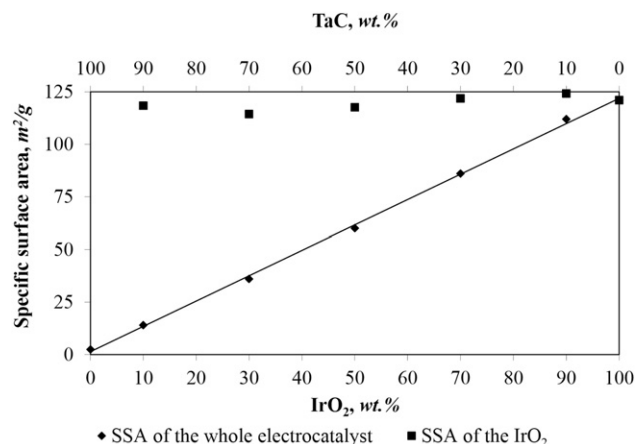


Fig. 6 – BET specific surface area of the prepared electrocatalysts.

crystallites are 1–2 orders of magnitude smaller than the agglomerates. Since no relation between SSA and crystallite size was found, it is concluded that the agglomerates are not porous and the adsorbent gas cannot access inner surfaces. Furthermore, with respect to the size variations observed (Fig. 3), it appears that crystallite size does not influence the shape and morphology of the agglomerates and, therefore, does not affect the SSA.

3.2.4. Powder conductivity

First of all, when comparing the presented results with published data it should be borne in mind that powder conductivity is strongly dependent on the conditions under which it is obtained. This is because the transition resistance between the individual powder particles plays a decisive role. From this, it follows that the most important aspect is particle dimensions and compressive force. Therefore, for instance, for bulk TaC a conductivity of $23\text{--}34 \times 10^3$ S/cm has been reported [13]. The conductivity of the as-received TaC powder used in this study was 118 S/cm. This difference is clearly due to the fact that TaC was used in powdered form. Compared to

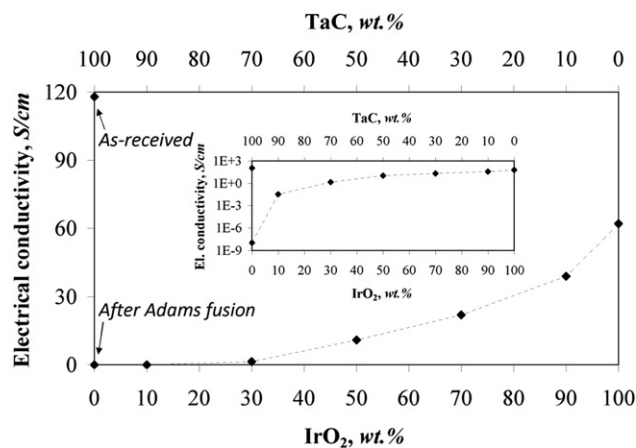


Fig. 7 – Powder conductivities of the prepared electrocatalysts. The inset graph shows conductivities with a logarithmically scaled y-axis.

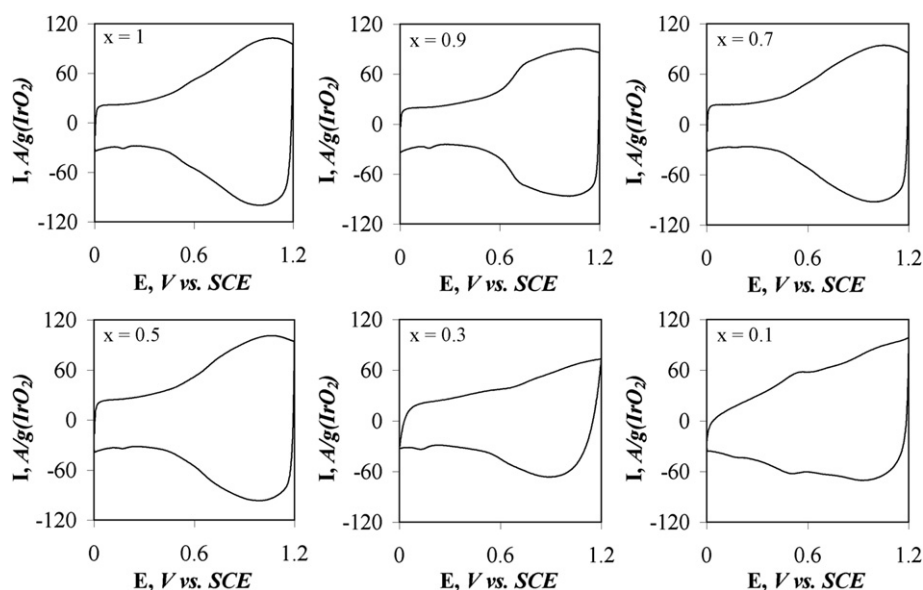


Fig. 8 – Cyclic voltammograms normalised to IrO_2 mass-specific current. Mass-based compositions correspond to general formula $(\text{IrO}_2)_x(\text{TaC})_{1-x}$. Potential sweep rate 500 mV/s, 0.5 M H_2SO_4 at room temperature.

pure IrO_2 powder, which had a conductivity of 62 S/cm, the as-received TaC powder was twice as conductive. Unfortunately, after synthesis, the conductivity of the TaC decreased by 10 orders of magnitude. Coming back to the above reported data, the drop in conductivity can be explained by the surface layer of a semiconductive NaTaO_3 formed during IrO_2 synthesis by Adams fusion. Since surface oxidation is directly linked to the use of this synthesis method, the employment of a different method may reduce or even prevent this drop in conductivity entirely. The dependence of materials-specific conductivity on its composition is summarised in Fig. 7. As shown in the logarithmic scale presented in the figure inset, the most pronounced conductivity increase occurs with the first IrO_2 addition to the support. This could be due to the interaction of the NaTaO_3 covering the support surface with Ir atoms, most probably directly during the fusion. Even though the increase in conductivity had already reached several orders of

magnitude at this stage, sufficient conductivity values of at least 10% of the conductivity of pure IrO_2 were first obtained with an IrO_2 content of 50 wt.%. This corresponds to the formation of a conductive IrO_2 film covering the surface of the support.

3.3. Electrochemical characterisation

3.3.1. Cyclic voltammetry

The cyclic voltammograms of the IrO_2 -based electrocatalysts (Fig. 8) had the overall shape that has been reported by other researchers [21,27]. This shape is characterised by an absence of any well-defined peaks, although the total anodic charge recorded is related to the total number of active sites [11]. A reliable, generally accepted electrochemical method of determining the active area, as it has for example been established for platinum, has not yet been found for iridium oxide.

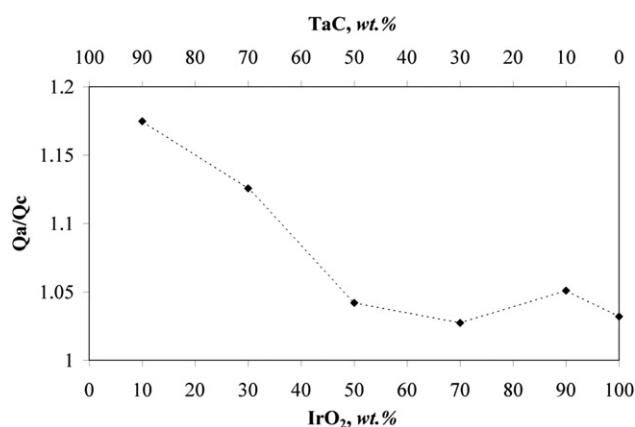


Fig. 9 – Ratio of anodic-to-cathodic charge between 0.4 and 1.2 V. Potential sweep rate 500 mV/s, 0.5 M H_2SO_4 at room temperature.

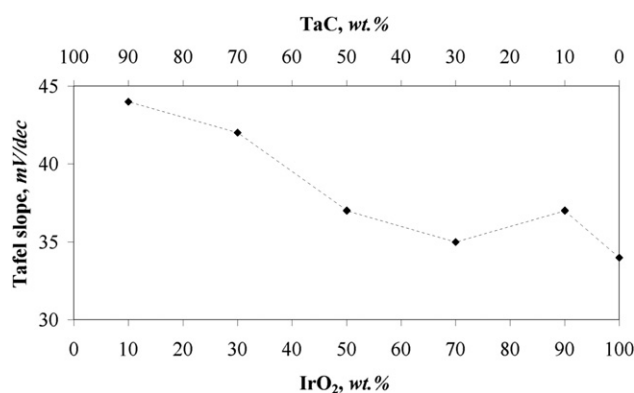


Fig. 10 – Tafel slopes of the prepared electrocatalysts. From linear part of the polarisation curve in Tafel plot between 1.1 and 1.3 V. Potential sweep rate 1 mV/s, 0.5 M H_2SO_4 at room temperature.

In the potential region between 0.4 and 1.2 V, the anodic and cathodic parts of the voltammograms display a high degree of symmetry. The predominant influence of IrO₂ on the voltammetric response of the electrode is indicated by the anodic-to-cathodic charge ratio (Q_a/Q_c) being close to unity [28]. In the present study this charge was integrated for the potential range between 0.4 and 1.2 V, where the polarisation curve is not influenced by gas evolution reactions or adsorption processes. Polarisation curves obtained at a scan rate of 500 mV/s were used to obtain higher current densities and thus a lower relative error of the experimental data. The results are summarised in Fig. 9. They are in agreement with the work of Marshall et al. [14], who observed that the higher the scan rate, the higher the differences between the charge ratios of the electrocatalysts being compared. In the present case, the ratio value was close to unity for electrocatalysts with ≥50 wt.% IrO₂. The ratio was very close to that of pure IrO₂. When the content of the IrO₂ was reduced below 50 wt.%, the ratio increased, indicating enhanced interaction of the support with the electrolyte. This result correlates well with the conductivity measurements.

3.3.2. Tafel experiments

Pseudostationary linear sweep voltammetry was used to determine the Tafel slopes for the individual electrocatalysts (Fig. 10). Tafel slopes are an indicator of electrocatalyst quality: the lower the Tafel slope, the faster the kinetics of the reaction and the more active the electrocatalyst (under constant electrocatalyst load conditions). Electrocatalyst activity towards oxygen evolution as a desired electrode reaction was measured.

In acidic electrolyte, several possible reaction mechanisms of the oxygen evolution reaction have been proposed [29,30]. The Tafel slope cannot be used to directly identify the reaction pathway, but it may be used to determine the rate-determining step in an assumed mechanism. However, this is not straightforward as the symmetry factor in the kinetic equations is usually not known and the considered value of 0.5 is not necessarily accurate under the conditions studied [30]. Moreover, in the present case the electrocatalysts consist of agglomerates. They probably have different reaction sites. Therefore, different rate-determining steps for different reaction sites can coexist and the measured Tafel slope then represents an average. A Tafel slope of 30 mV/dec points to the second step in the “oxide path”, reaction (2) [31], and a Tafel slope of 40 mV/dec suggests that the second step in the “electrochemical oxide path”, reaction (4) [31], is rate-determining.

Oxide path [30]:

- (1) $S + H_2O \rightarrow S-OH + H^+ + e^-$
- (2) $2S-OH \rightarrow S-O + S + H_2O$
- (3) $2S-O \rightarrow 2S + O_2$

The electrochemical oxide path has identical steps (1) and (3). It differs in step (2), which in this case can be described by reaction (4) [30]:

- (4) $S-OH \rightarrow S-O + H^+ + e^-$

Again, when the IrO₂ content ranged from 50 to 100 wt.%, the Tafel slopes obtained were similar for all electrocatalysts under study (34–37 mV/dec). But when the IrO₂ concentration was 10 or 30 wt.%, the Tafel slope increased to above 40 mV/dec, indicating a different rate-determining step. This increase correlates with the conductivity and cyclic voltammetry measurements. A similar effect was also observed by Marshall et al. [14].

4. Conclusions

In this study it has been shown that TaC represents a promising candidate for application as an IrO₂ electrocatalyst support for the anodic oxygen evolution reaction in the PEMWE. The negative aspect represented by the formation of a surface film of NaTaO₃, characterised by low conductivity, may be overcome by applying a sufficient amount of IrO₂, in this particular case 50 wt.% or more. Such a supported electrocatalyst shows properties similar to those of pure IrO₂, including electrocatalytic activity and the rate-determining step of the oxygen evolution reaction. The inertness of the support to the environment in electrocatalysts with IrO₂ content of 50 wt.% or more is further confirmed in cyclic voltammetry experiments by the ratio of pseudocapacitive charge passed through the electrode being very close to the value of pure IrO₂. The prepared electrocatalysts have to be tested in a PEMWE to confirm their properties under conditions of a real water electrolysis process.

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